# CONVERSION PRODUCTS FROM TRIETHANOLAMINE UNDER VINYLATION REACTION CONDITIONS AND THEIR ANALYSIS

S.A. Ostrovskii, L.A. Ustynyuk,
N.F. Kononov, I.A. Chekulaeva,
Ya.I. Makarovskii, Ya.I. Levikov,
and G.S. Panova

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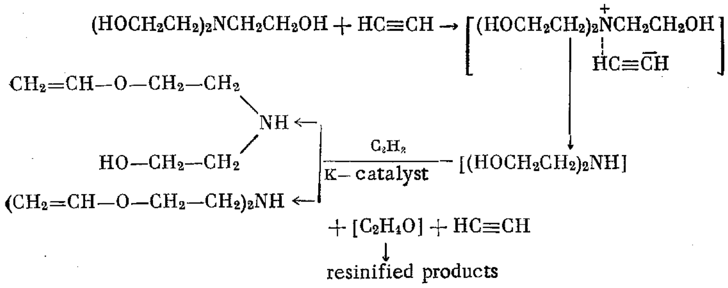
A method developed by us for the chromatographic analysis of the reaction mixture formed in the process of vinylation of triethanolamine has enabled new data to be obtained concerning this process. Besides the mono-, di-, and trivinyl ethers of triethanolamine, a number of other substances have been detected on chromatograms of the reaction mixture (Fig. 1) obtained under high [1] and low [2, 3] pressure acetylene conditions.

By comparison with standard samples by a GLC method we have shown the presence in the reaction mixture of significant quantities (7-10%) of the mono- and divinyl ethers of diethanolamine; this is unexpected since 95-99% triethanolamine was subjected to vinylation. Additional evidence for the presence of diethanolamine vinylation products in the reaction mixture and also data indicating the presence of the vinyl ether of N-hydroxyethylmorpholine (7-10%) in the reaction products were obtained by chemical analysis of the fractions containing substances of lower boiling point than the vinyl ethers of triethanolamine. One of these substances was the divinyl ether of diethanolamine; this was demonstrated by its use as amino component in the Mannich reaction and conversion into bis(vinyloxyethyl)butyloxymethylamine and bis[di(vinyloxyethyl)]methylenediamine by the method in [4] and also by its conversion into the known N-acetoxy derivative [5]. The structure of the vinyl ether of N-hydroxyethylmorpholine was assigned to the other substance on the basis of the elemental analysis results and the data from the IR spectra.

The mechanism of formation of the vinyl ethers of diethanolamine in the process of vinylation of triethanolamine is not fully explained although undoubtedly it includes the rupture of a C—N bond in the triethanolamine molecule. Examples of the rupture of C—O and C—S bonds in glycols and thioglycols under vinylation conditions are known in the literature [6, 7] and the C—N bond in its stability occupies an intermediate position between these bonds [8]. One of the possible routes for the formation of vinyl ethers of diethanolamine is given in the scheme



The formation of the vinyl ether of N-hydroxyethylmorpholine in the course of the reaction under study can be explained in two ways: by the dehydration of triethanolamine and subsequent vinylation of

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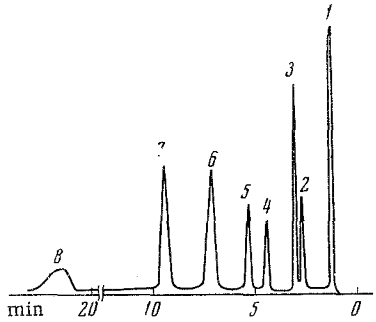

Fig. 1. Chromatogram of the reaction mixture formed by the vinylation of triethanolamine: 1) solvent; 2) divinyl ether of diethanolamine; 3) vinyl ether of N-hydroxyethylmorpholine; 4) monovinyl ether of diethanolamine; 5) trivinyl ether of triethanolamine; 6) $\alpha$-pyrrolidone (internal standard); 7) divinyl ether of triethanolamine; 8) monovinyl ether of triethanolamine.

N-hydroxyethylmorpholine or by the dehydration of the monovinyl ether of triethanolamine. Examples of a similar type are known with the conversions of certain N-alkyl- and N-aryldihydroxydialkylamines (for example, N, N-dihydroxyethyl aniline) into the corresponding morpholine derivatives under the influence of a high temperature [9].

## EXPERIMENTAL

Chromatographic Analysis of the Vinylation Products of Triethanolamine. The chromatographic analysis of the reaction mixture was carried out on an LKhM-5 SKB IOKh instrument with a katharometer detector. The analysis conditions were: stationary phase polyethylene glycol 40,000 as a 20% coating on Chromosorb-W previously treated with 1% alcoholic KOH solution; stainless steel column of length 2.5 m and internal diameter 4 mm; carrier gas He; carrier gas flow rate 60 cm$^3$/min, analysis temperature 230°C; $\alpha$-pyrrolidone was used as internal standard.

Synthesis of Bis(vinyloxyethyl)butyloxymethylamine (I) and Isolation of the Vinyl Ether of N-Hydroxyethylmorpholine (II). Vacuum distillation of 420 g of reaction mixture yielded 80 g of a fraction with bp 66-67.0° (1 mm). To 39.3 g of this fraction was added 11.1 g of n-butyl alcohol, 3 g of paraform, and 50 ml of benzene, the mixture was boiled with water entrainment until the distillation of water ceased. After cooling, the obtained reaction mixture was washed with aqueous NaHSO$_3$ solution in order to remove unreacted formaldehyde and then subjected to vacuum distillation. This gave 17 g (50% yield) of (I), bp 91-92° (0.5 mm); $n_D^{20}$ 1.4525 and 11.8 g (50%) (II), bp. 66-67.0° (1 mm); 74-74.5° (2.5 mm); $n_D^{20}$ 1.4675 (according to the data in [10]: bp 208.9-209.3° (751 mm); $n_D^{20}$ 1.4680; [11]: bp 53-54° (0.9 mm); $n_D^{25}$ 1.4658). For the latter was found: C 61.76; H 9.65; N 9.05%. $C_8H_{15}NO_2$. Calculated: C 61.15; H 9.56; N 8.91. In the IR spectrum there are characteristic absorption bands in the regions 1050-1150, 1203, 1623-1644, and 3115 cm$^{-1}$ which correspond with the vibrations of the C—O—C—, =C—O—, C=C—, and =CH— bonds respectively.

Synthesis of Bis[di(vinyloxyethyl)]methylenediamine (III) and Isolation of the Vinyl Ether of N-hydroxyethylmorpholine (II). To 39.3 g of the fraction with bp 66-67° (1 mm) was added 12 g of paraform and 50 ml of dioxane. The mixture was heated for 4 h at 70-80°, washed with aqueous NaHSO$_3$ solution, and subjected to vacuum distillation. This gave 10 g (35%) of (III), bp 155-160° (1 mm); $n_D^{20}$ 1.4770 and 18.9 g (89%) of (II).

Preparation of Divinyl Ether of N-Acetyldiethanolamine (IV). The synthesis of (IV), bp 120-121° (4 mm); $n_D^{20}$ 1.4778 was carried out by reacting the divinyl ether of diethanolamine with acetyl chloride in the presence of pyridine.

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## CONCLUSIONS

1. A method has been developed for GLC analysis of the reaction mixture formed by the vinylation of triethanolamine; the method can be used while carrying out the processes of synthesis and separation of the vinyl ethers of triethanolamine.

2. By combining the chemical and GLC analysis of this reaction mixture the presence of anomalous products of the conversion of triethanolamine under vinylation conditions has been demonstrated; these

products are the mono- and divinyl ethers of diethanolamine and the vinyl ether of N-hydroxyethylmorpholine; the total content of these is 14-20% and is dependent on the conditions for carrying out the process.

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